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CATHOLIC UNIV OF AMERICA WASHINGTON DC DEPT OF PHYSICS

F/B 20/13

A NEW APPROACH TO KINETICS OF SPINODAL DECOMPOSITION IN THE Li-N-ETC(U)

AUG 80 Y M WONG, P H MEIJER

N00014-78-C-0518

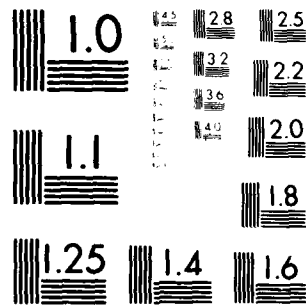
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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 3	2. GOVT ACCESSION NO. AD A089247	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) A new approach to Kinetics of Spinodal Decomposition in the linear regime		5. TYPE OF REPORT & PERIOD COVERED Technical Report
7. AUTHOR(s) Y. M. Wong Paul H. E. Meijer		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS The Physics Department The Catholic University of America Washington, D. C. 20064		8. CONTRACT OR GRANT NUMBER(s) ONR-N00014-78-C-0518
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Arlington, Virginia 22217		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE August 28, 1980
LEVEL		13. NUMBER OF PAGES 30
		15. SECURITY CLASS. (of this report) Unclassified
16. DISTRIBUTION STATEMENT (of this Report) This document has been approved for public release and sale; its distribution is unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Spinodal, Cahn-Hilliard eg., Landau-Ginsburg eg., Molecular Dynamics, Cluster size Continuous Time Random Walk, Generalized Master Equation.		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) We generalized the unified approach of Metiu, Kitahara and Ross and are able to make new predictions about the early stage of the unstable fluctuation.		

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

Errata

- On page 4: there should be a '-' sign in front of M (1.7)
- On page 22: 8 lines from the top, $\psi(k) = a^2/(a^2 + k^2)$ instead of $\psi(k) = a^2$;
8 lines and 2 lines from the bottom a negative sign should be added in front of W_k
- On page 24: 5 Lines from the top W_k is to be replaced by $-W_k$
- On page 28: Ref. 23 should be "in Dynamical Critical Phenomena and Related Topics" Proc,

9 Technical Report No. 3

Office of Naval Research; Contract ¹⁵ N00014-78-C-0518

6 A New Approach to
Kinetics of Spinodal Decomposition
in the linear regime.

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I. Introduction and summary of previous works

Phase separation occurs when a two component system is quenched below a certain critical temperature T_c . Depending on the depth of quenching and the initial composition, this process of unmixing can either take place in a thermodynamic metastable region i.e., nucleation or in a thermodynamic unstable region i.e., spinodal decomposition (See Fig. 1), and this latter one will be the theme of our investigation.

The thermodynamics of phase separation is assumed ¹ to be governed completely by the existence of a coarse-grained free energy density functional $F[n]$ which is given by

$$e^{-\beta F[n]} = \sum_{\substack{[\text{constrained}] \\ [\text{phase space}]}} e^{-\beta H} \quad (1.1)$$

and is to be identified with the Wilson-fixed point hamiltonian².

We give here a brief summary of the work by Cahn ³. The gradient of this free energy functional w.r.t. the density is postulated to represent a kind of generalized thermodynamic chemical potential μ

$$\mu = \frac{\delta F}{\delta n} \quad (1.2)$$

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which then drives a current i.e.

$$\vec{j} = M \nabla \mu \quad (1.3)$$

Since there is no source or a sink possible in the process of quenching one can also write down the conservation law which governs the time-dependence of the current

$$\frac{\partial n}{\partial t} + \nabla \cdot \vec{j} = 0 \quad (1.4)$$

Expressions (2) to (4) therefore constitute a theory for the kinetics of phase separation once the functional form of $F[n]$ is either derived from (1) or postulated by some physical arguments. The final equation of interest is the usual Cahn-Hilliard eqn. (CH),

$$\frac{dn(\vec{r}, t)}{dt} = -M \nabla^2 \frac{\delta F}{\delta n} \quad (1.5)$$

where one has also assumed that the mobility M , is spatially independent.

$F[n]$ is usually an arbitrary power series expansion in n and Eqn (5) therefore is a nonlinear differential eqn for $n(\vec{r}, t)$. We will only be interested in the linear regime when $n(\vec{r}, t)$ deviates very little from the homogeneous phase n_0 , so that we only examine

the linear approximation to eqn (5). For the long time non-linear evolution, Langer and coworkers ⁴ have given a detail study.

Even in this linear regime or early stage of spinodal decomposition, five groups of workers deserve a brief mention.

(I) Cahn-Hilliard ⁵ have assumed the following specific form of the $F[n]$

$$F[n] = \int d\vec{r} \left[\frac{1}{2} K (\nabla n)^2 + f[n] \right] \quad (1.6)$$

which when substituted into (1.5) and after linearization, leads to

$$\frac{dn}{dt} = M \nabla^2 \left[-K \nabla^2 + \left. \frac{\partial^2 f}{\partial n^2} \right|_0 \right] n \quad (1.7)$$

This has a solution of the form $e^{-i\vec{k} \cdot \vec{r} - w_k t}$ with w_k given by

$$w_k = M k^2 \left[K k^2 + \left. \frac{\partial^2 f}{\partial n^2} \right|_0 \right] \equiv M K k^2 [k^2 - k_c^2] \quad (1.8)$$

and since $\left. \frac{\partial^2 f}{\partial n^2} \right|_0$ is negative in the unstable region, so for

$$k^2 < k_c^2 \equiv \left| \frac{1}{K} \left. \frac{\partial^2 f}{\partial n^2} \right|_0 \right| ,$$

the $n_k(t)$ grows exponentially. But only the k^{th} component near $k_m = k_c/\sqrt{2}$ will dominate the others as a result of two competing processes:

(1) The clustering forces, $Kk^2 + \left. \frac{\partial^2 F}{\partial n^2} \right|_0$, which favour decomposition at small k , i.e. the smaller the k -value the larger w_k and

(2) The diffusion limitation, the k^2 factor in front of $Kk^2 + \left. \frac{\partial^2 F}{\partial n^2} \right|_0$ which slows the decomposition rate at small k .

By plotting $-w_k/k^2$ vs k^2 , eqn (1.8) predicts a linear curve shown in Fig. 2. Experimentally the decomposition rate rises much more slowly than exponentially, i.e. the measured $-w_k/k^2$ versus k^2 exhibit marked upward curvature. Also observed is the fact that the value of k_m decreases with time, which is identified with the process of coarsening in the early stages of the decomposition.

(II) Evans and Telo da Gama ⁶ propose a functional Taylor series expansion of $F[n]$ i.e.

$$F[n] \approx F[n_0] + \mu[n_0] \int d\vec{r} \tilde{n}(\vec{r}) + \frac{1}{2} \iint d\vec{r} d\vec{r}' \left. \frac{\delta^2 F}{\delta n(\vec{r}) \delta n(\vec{r}')} \right|_0 \tilde{n}(\vec{r}) \tilde{n}(\vec{r}') \quad (1.9)$$

instead of (1.6). Their main contribution is that they are able to provide a theory for spinodal decomposition without additional parameter such as K and $\left. \frac{\partial^2 F}{\partial n^2} \right|_0$ in (1.7) by identifying $\left. \frac{\delta^2 F}{\delta n(\vec{r}) \delta n(\vec{r}')} \right|_0$ with the direct correlation function $c(r)$ i.e.

$$\left. \frac{\delta^2 F[n]}{\delta n(\vec{r}) \delta n(\vec{r}')} \right|_0 = \frac{1}{\beta} \left[\frac{\delta(\vec{r} - \vec{r}')}{n_0} - c(|\vec{r} - \vec{r}'|) \right] \quad (1.10)$$

which is to be calculated from the Percus-Yevick approximation⁷. In particular, if one expands the Fourier transform of $c(r)$ i.e. $c(k)$ in powers of k^2 , one obtains for the long wavelength composition fluctuation the original Cahn-Hilliard result. Indeed a curvature is predicted from such a microscopic theory which also agrees with the following treatment of Abraham and coworkers.⁸

(III) In this generalised van der Waals theory⁸, the free energy is related to the variation in density through the product of the interparticle potential $u(r)$ and the uniform pair correlation function $g_0(r)$: in the case of 1-dimension, one has

$$f(z) = f_0[n(z)] + \pi n(z) \int_{-\infty}^{\infty} dw [n(z+w) - n(z)] \int_{|w|}^{\infty} d\xi \xi u(\xi) g_0(\xi, [n(z)]) \quad (1.10)$$

With the same argument, one is led to

$$w_k = Mk^2 \left[\left. \frac{\partial^2 f}{\partial n^2} \right|_0 + 4\pi \int_0^{\infty} dw \Omega_0(w) [\cos kw - 1] \right] \quad (1.11)$$

where $\Omega_0(w)$ is determined by $u(r)$ and $g_0(r)$. One can evaluate $\Omega_0(w)$ by numerical method as done by Evans et. al⁶ for a L-J potential, and obtain a similar upward curvature in the following suggested procedure⁸: the time-dependent structure factor is computed by MD⁸ one then relates the w_k through

(IV) Cook's⁹ intensity equation

$$S(k, t) = \left[S(k, 0) + \frac{Mk^2}{\beta w_k} \right] e^{2w_k t} - \frac{Mk^2}{\beta w_k} \quad (1.12)$$

which takes into account the interaction between the system and the surrounding reservoir by adding a Langevin¹⁰ noise term $F(t)$ to equation (1.5) and $F(t)$ is assumed to have a zero means

$$\langle F(\vec{r}, t) \rangle = 0 \quad (1.13a)$$

and a white noise spectrum

$$\langle F(\vec{r}, t) F(\vec{r}', t') \rangle = - \frac{4}{\beta} M \nabla^2 \delta(\vec{r} - \vec{r}') \delta(t - t') \quad (1.13b)$$

It is to be remarked that the curvature which follows from Abraham's generalised van der Waals theory⁸ has a dynamical origin whereas the curvature which follows from Cook's fluctuation theory⁹ has a statistical origin but they are acting cooperatively and are of the same sign so it is a problem to observe these two effects separately experimentally.

(V) The last approach is due to Nonnenmacher¹¹ who starts out with a Boltzmann equation which is solved in the relaxation time approximation. Crucial to this approach in addition to the nonzero value of the relax time τ is the introduction of a time and spatial dependence of the local equilibrium distribution through a local chemical potential $\mu(\vec{r}, t)$ which as expected is to be related to the free energy density functional. By applying a perturbation expansion he obtains

$$\left(1 + \tau \frac{\partial}{\partial t}\right) \frac{\partial}{\partial t} = M \nabla^2 \left[\frac{\delta F}{\delta n} - K \nabla^2 n \right] \quad (1.14)$$

in the lowest order. This equation reduces to the Cahn-Hilliard equation when $\tau \rightarrow 0$, otherwise it gives rise to

$$\omega_k (1 + \tau \omega_k) = -M k^2 \left[\left. \frac{\partial^2 f}{\partial n^2} \right|_0 + K k^2 \right] \quad (1.15a)$$

or

$$\omega_k^{\pm} = \frac{1}{2\tau} \left[-1 \pm \sqrt{1 + 4\tau M k^2 (k_c^2 - k^2)} \right] \quad (1.15b)$$

The k_m and k_c are the same as given by Cahn-Hilliard equation. But there is one additional branch of ω_k whose physical meaning has not been explored. The plot of $-\omega_k/k^2$ vs. k^2 for all theories are shown in Fig. 3 for comparison:

(VI) We now introduce a unified description of phase separation due to Metiu, Kitahara and Ross.¹² Their starting point is a Markoffian master equation for the probability that the density $n(\vec{r}, t)$ has certain values at time t i.e.

$$\tau \frac{\partial P(n, t)}{\partial t} = \sum_a \left[W(n-a \rightarrow n) P(n-a, t) - W(n \rightarrow n+a) P(n, t) \right] \quad (1.16)$$

where τ defines a characteristic time scale and the time-independent transition rate is postulated to be given by

$$W(n \rightarrow n+a) = \frac{1}{(2\pi)^{M/2}} \frac{1}{(\det \Delta)^{M/2}} e^{-\frac{1}{2} \langle a | \frac{1}{\Delta} | a \rangle} e^{-\frac{\beta}{2} [F(n+a) - F(n)]} \quad (1.17)$$

The first factor accounts for the fact that deviation in density in different space points are correlated through the correlation matrix $\frac{1}{\Delta}$ and Δ also serves as a cut off to prohibit those unlikely large deviations. The second factor tends to account for the fact that changes in density which cause an increase in the free energy density functional is less probable thermodynamically. It can be shown that

$$\begin{aligned} \langle a_i a_j \rangle &\equiv \int d\vec{a} \, a_i a_j \frac{1}{(2\pi)^{M/2}} \frac{1}{(\det \Delta)^{M/2}} e^{-\frac{1}{2} \langle a | \frac{1}{\Delta} | a \rangle} \\ &= \Delta_{ij} \end{aligned} \quad (1.18)$$

which can be split into two parts i.e.

$$\Delta_{ij} = \langle a_i^2 \rangle [\delta_{ij} - \phi_{ij}] \equiv R [\delta_{ij} - \phi_{ij}] \quad (1.19)$$

where $\phi_{ij} = 0$ for $i = j$ and $\sum_j \phi_{ij} = 1$. ϕ_{ij} is the correlation of changes in density in two spatial points i and j .

By applying Feynman's path integral method¹³, MKR are able to derive a Langevin equation for $n_i(t)$, the density of the i^{th} cell at time t

$$\frac{\partial n_i(t)}{\partial t} + \frac{\beta}{2c} \sum_{j=1}^M \Delta_{ij} \frac{\delta F[n]}{\delta n_j} = 0 \quad (1.20)$$

with the choice of

$$\phi_{ij} = \frac{1}{(2\pi\lambda)^{3/2}} e^{-\frac{(\lambda-i)^2}{2\lambda^2}} \quad (1.21)$$

and taking the continuum limit, they arrive at

$$\frac{\partial n(\vec{r}, t)}{\partial t} = - \frac{\beta R}{2\tau} \left[1 - e^{-\frac{\lambda^2}{2} \nabla^2} \right] \frac{\delta F}{\delta n} \quad (1.22)$$

Immediately they show that in a linear theory (i) if $\lambda^2 \nabla^2 / 2 \rightarrow \frac{\lambda^2 k^2}{2}$ is small (1.22) reduces to the C-H equation and (ii) if λ is large, $\phi_{ij} \rightarrow 0$ and one obtains

$$\frac{\partial n}{\partial t} = - \frac{\beta R}{2\tau} \frac{\delta F}{\delta n} \quad (1.23)$$

which is the Landau-Ginsburg equation for nucleation. That is the reason why equation (1.22) offers a unifying description of phase separation in the early stage or linear regime.

Our investigation will take (1.22) as the point of departure. We will clarify the meaning of ϕ_{ij} and hence of λ , in both (1.21) and in (1.22). This simple procedure will give rise to an additional curvature for the $-w_k/k^2$ versus k^2 plot due to the finiteness of λ . Next we will generalise (1.20) to take care of a much shorter time behaviour of $n(\vec{r}, t)$. Unfortunately the complete dynamics is too complicated so we have to be satisfied making some plausible assumptions and postulations. These allow one to give several new predictions. One of them coincides with the Boltzmann equation approach of Nonnenmacher¹¹. Others seem to predict a new dependence of w_k at small k and also possibly a new time dependence of w_k which is in qualitative agreement with the work by Kawasaki

and coworker.¹⁴

II. Existence of Additional curvature

Rewriting (1.22) here for convenience

$$\frac{dn(\vec{r}, t)}{dt} = - \frac{\beta R \lambda^2}{4\tau} \left\{ \frac{1 - e^{-\frac{\lambda^2}{2} \nabla^2}}{\frac{\lambda^2}{2}} \right\} \frac{SF}{\delta n} \quad (2.1)$$

and if one defines $M \equiv \frac{\beta R \lambda^2}{4\tau}$, then (2.1) has a solution of the form $e^{-w_k t}$ where

$$w_k^{MKR} = \left\{ \frac{1 - e^{-\frac{\lambda^2 k^2}{2}}}{\frac{\lambda^2 k^2}{2}} \right\} w_k^{OLD} \quad (2.2)$$

It is trivial to show from (2.2) that if $\lambda^2 k^2 / 2$ is very small $w_k^{MKR} \rightarrow w_k^{old}$, whereas if $\lambda^2 k^2 / 2$ is not too small, the bracket on the RHS of (2.2) will be the correction term whose zeroth order is just 1 etc. as shown in Fig. 4

Next we want to discuss¹⁵ the physical meaning of λ . Since it occurs in the correlation matrix ϕ_{ij} for distinct cells as a cut off we argue that λ is the linear dimension or a characteristic length scale which will connect two points in the space such that any changes of density in one point is due to changes in other points within the dimension so λ expresses the range where

conservation law in number of particles has to be held and this conservation law thus gives rise to correlation which affects the kinetics of phase separation.

For a specific system λ is fixed. If the mechanism which gives rise to phase separation has a longer characteristic length ℓ i.e. $\ell \gg \lambda$ then the change in density can be effected without local conservation law; mathematically this is represented by the fact that $\phi_{ij} \rightarrow 0$ as $\ell^2/\lambda^2 \rightarrow \infty$ and one has a GL equation. On the other hand if $\lambda \gg \ell$ for a rather different kind of mechanism which initiates the phase separation then Cahn-Hilliard equation should be used to describe the situation.

An alternate criterion¹² is to examine the size of the cluster Δx compared with the correlation length λ . Since $k \sim \frac{1}{\Delta x}$, then if $\lambda k \approx \frac{\lambda}{\Delta x}$ is small the C-H equation applies and if $\lambda k \approx \frac{\lambda}{\Delta x}$ is large the GL equation applies and finally when $\lambda \sim \Delta x$, one should use the MKR equation. For phase separation $\Delta x \sim 10A$, as said in MKR; in the case of condensation in a gas $\lambda \approx 10^2$ to $10^3 A$, hence one uses the GL equation whereas in the case of a fluid, $\lambda \approx 1A$ hence the CH equation applies.

III. Formal generalization of (1.20)

Let $n(\vec{r}, t)$ be the deviation of density at point \vec{r} and at time t . (1.2) can be generalised to:

$$\frac{dn(\vec{r},t)}{dt} = - \frac{\beta}{2\tau} \int d\vec{r}' \int dt' \langle n(\vec{r},t) n(\vec{r}',t') \rangle \frac{\delta F[n]}{\delta n(\vec{r}',t')} \quad (3.1)$$

since we conclude from Section II that $\Delta_{ij} = \langle n_i n_j \rangle$ is a spatial correlation between changes in density between i^{th} and j^{th} cell. The above takes into account additional time correlation in this change in density. Observe that (3.1) relates $n(\vec{r},t)$ to a higher order correlation $\langle n(\vec{r},t) n(\vec{r}',t') \rangle$ and therefore it is essentially the first member of a hierarchy of transport equation which is a unique feature of a many-body coupled system. The exact solution (if it exists) amounts to solving the Liouville equation.⁷

The above generalization is made also plausible when one gains some experience in converting a purely dissipative equation for the velocity field of a fluid

$$\frac{d\vec{v}(t)}{dt} = -\gamma \vec{v}(t) + F(t) \quad (3.2a)$$

into the following non-local equation of motion for $\vec{v}(t)$

$$\frac{d\vec{v}(t)}{dt} = - \int_0^t dt' \psi(t-t') \vec{v}(t') + F(t) \quad (3.3b)$$

in the Langevin equation approach to Brownian motion¹⁰ where $\psi(t)$, the relaxation function, which represents a better description for the process in a shorter time regime. This is proved trivially by letting $\psi(t) = 2\gamma \delta(t)$ in (3.3b) and one obtains (3.2a) immediately. $1/\gamma$ here can be identified as the relaxation time for the velocity of the Brownian particle.

We will now make two crucial assumptions which cannot be verified so far and which are the spatial and time translational invariances of the system, i.e.

$$\langle n(\vec{r}, t) n(\vec{r}', t') \rangle \equiv \langle n(\vec{r} - \vec{r}') n(t - t') \rangle \quad (3.4)$$

which is true only for equilibrium state. Next we approximate the RHS of (3.4) by products of spatial and time correlation function i.e.

$$\langle n(\vec{r} - \vec{r}') n(t - t') \rangle \equiv \psi(\vec{r} - \vec{r}') \psi(t - t') \quad (3.5)$$

In the limiting case when $\psi(t) = 2\delta(t)$, (3.1), (3.4) and (3.5) together imply the MKR equation. We will study various possible forms of $\psi(\vec{r})$ and $\psi(t)$. It is to be noted that $\psi(\vec{r})$ and $\psi(t)$ are distribution in step length and waiting time for the change of the density variable $n(\vec{r}, t)$ and not for $P(n, t)$ in (1.16). We will first consider $\psi(t)$ in section IV and $\psi(\vec{r})$ in section V and discussion will constitute the final section.

(IV) Generalization of MKR equation in the time domain

In this section we keep ϕ_{ij} equal to $\frac{1}{(v\tau\lambda)^{3/2}} e^{-\frac{(i-j)^2}{2\lambda^2}}$ and let $\psi(t)$ assume different forms. In general:

$$\frac{dn(\vec{r}, t)}{dt} = \int_0^t dt' \psi(t - t') \left[-\frac{\beta}{2\tau} \int d\vec{r}' \psi(\vec{r} - \vec{r}') \frac{\delta F}{\delta n(\vec{r}', t')} \right] \quad (4.1)$$

After linearization, one Fourier transforms (4.1) to obtain

$$\frac{dn_k}{dt} = \int_0^t dt' \psi(t-t') w_k n_k(t') \quad (4.2)$$

where w_k is the rate of decomposition of the k^{th} component fluctuation as given by previous approaches. Taking Laplace transform of (4.2) one obtains in the Laplace variable

$$\tilde{n}_k(\epsilon) = \frac{n_k(0)}{\epsilon + \tilde{\psi}(\epsilon) w_k} \quad (4.3)$$

where $\tilde{f}(\epsilon) \equiv \int_0^\infty dt e^{-\epsilon t} f(t)$ is the Laplace transform of $f(t)$. Various forms of $\psi(t)$ are studied below:

(1) when $\psi_1(t)$ is of the form $\delta(t)$, $\tilde{\psi}_1(\epsilon) = 1$ and one recovers C-H equation from (4.3).

(2) When $\psi(t)$ is given by

$$\psi_2(t) = \alpha e^{-\alpha t} \quad (4.4)$$

then one notices that in the limit $\alpha \rightarrow \infty$, $\psi_2(t) \rightarrow \psi_1(t)$. In general for finite α , $\tilde{\psi}_2(\epsilon) = \alpha/(\epsilon + \alpha)$ and (4.3) becomes

$$\begin{aligned} \frac{\tilde{n}_k(\epsilon)}{n_k(0)} &= \frac{1}{\epsilon + \frac{\alpha}{\epsilon + \alpha} w_k} = \frac{\epsilon + \alpha}{\epsilon^2 + \alpha\epsilon + \alpha w_k} \quad (4.5) \\ &\equiv \frac{\epsilon + \alpha}{(\epsilon - \epsilon_1)(\epsilon - \epsilon_2)} \end{aligned}$$

where

$$\epsilon_{\frac{1}{2}} = -\frac{\alpha}{2} \pm \frac{1}{2} \sqrt{\alpha^2 - 4\alpha\omega_k} \quad (4.6)$$

$$\frac{\eta_k(t)}{\eta_k(0)} = \frac{\frac{\alpha}{2} + \frac{1}{2} \sqrt{\alpha^2 - 4\alpha\omega_k}}{\sqrt{\alpha^2 - 4\alpha\omega_k}} e^{\lambda \left(-\frac{\alpha}{2} + \frac{1}{2} \sqrt{\alpha^2 - 4\alpha\omega_k} \right)} + \left[\frac{\frac{\alpha}{2} - \frac{1}{2} \sqrt{\alpha^2 - 4\alpha\omega_k}}{-\sqrt{\alpha^2 - 4\alpha\omega_k}} \right] e^{\lambda \left(-\frac{\alpha}{2} - \frac{1}{2} \sqrt{\alpha^2 - 4\alpha\omega_k} \right)} \quad (4.7)$$

which is identical with the two possible solutions given by Nonnenmacher¹¹ if one can identify α with $1/\tau$.

To facilitate this identification we have to make contact with the Continuous Time Random Walk (CTRW) model of stochastic processes of Montroll and Weiss¹⁶. According to their modelling of a stochastic process in transport theory there are two important probability distributions: one for the step length $p(l - l')$ and one for the waiting time distribution $\psi(t - t')$. This latter one determines how long the walker will remain in a site before it jumps to another site. The usual form taken is the above exponential distributed time function. But it is also obvious that a probability distribution that changes with a constant rate α in a short duration is of an exponential form $e^{-\alpha t}$:

$$p(t + \Delta t) = p(t) - \alpha p(t) \Delta t$$

$$\rightarrow p(t) = p(0) e^{-\alpha t}$$

Now if we represent a state by the occupancy of the site by the walker, then the state disappears or relaxes in a rate α if the walker has a $\alpha e^{-\alpha t}$ waiting time distribution.

To proceed further on with other possible form of $\psi(t)$, we want to recall the relation between CTRW and the Generalised Master Equation (GME) for the probability distribution for $P(m, t)$ in the theory of exciton transport.¹⁷ In the latter theory one has

$$\frac{dP_m}{dt} = \int_0^t dt' \left[\sum_n W_{mn}(t-t') P_n(t') - W_{nm}(t-t') P_m(t') \right] \quad (4.8)$$

where $W_{mn}(t)$ is the memory function for any transition between the m^{th} and n^{th} sites. It can be shown that¹⁷ when $W_{mn}(t) = F_{mn} \phi(t)$ and $F_{mm} = F[\delta_{m, n+1} + \delta_{m, n-1}]$, (4.8) becomes the ordinary diffusion equation if $\phi(t) = \delta(t)$; it becomes the wave equation if $\phi(t) = c \theta(t)$ and it becomes the telegraph equation if $\phi(t) = ce^{-\alpha t}$. It is pointed out that¹⁶ signal propagation in extremely short time can be described by the wave equation whereas for long time, the signal propagates diffusively and in the intermediate regime its propagation is governed by the telegraph equation.

It is further demonstrated¹⁷ that for a time and spatial invariant system, the waiting time distribution $\psi(t)$ in a CTRW is related to the memory function $\phi(t)$ of the GME by

$$\tilde{\psi}(\epsilon) = \frac{\tilde{\phi}(\epsilon)}{\epsilon + \tilde{\phi}(\epsilon)} \quad (4.9a)$$

or conversely

$$\tilde{\phi}(\epsilon) = \frac{\epsilon \tilde{\psi}(\epsilon)}{1 - \tilde{\psi}(\epsilon)} \quad (4.9b)$$

It is therefore natural to let $\psi(t)$ have the form:^{16,17}

$$\psi_3(t) = \frac{a}{\sqrt{\lambda^2 - 4a}} e^{-\frac{\lambda t}{2}} \left[e^{\frac{t}{2} \sqrt{\lambda^2 - 4a}} - e^{-\frac{t}{2} \sqrt{\lambda^2 - 4a}} \right] \quad (4.10)$$

where $\lambda^2 > 4a$ since this $\psi_3(t)$ will correspond to $\phi(t) = a e^{-\lambda t}$ which gives rise to a telegraph equation which is capable of describing both wave and diffusive motion. Here the former type of motion represents a better description in the short time regime not probed by the latter type of description. Preliminary calculations give three possible roots to $n_k(t)$:

$$\frac{n_k(t)}{n_k(0)} = e^{\frac{\epsilon_1 t}{\epsilon_1 - \epsilon_2}} \frac{\epsilon_1^2 + \lambda \epsilon_1 + a}{(\epsilon_1 - \epsilon_2)(\epsilon_1 - \epsilon_3)} + e^{\frac{\epsilon_2 t}{\epsilon_2 - \epsilon_1}} \frac{\epsilon_2^2 + \lambda \epsilon_2 + a}{(\epsilon_2 - \epsilon_1)(\epsilon_2 - \epsilon_3)} + e^{\frac{\epsilon_3 t}{\epsilon_3 - \epsilon_1}} \frac{\epsilon_3^2 + \lambda \epsilon_3 + a}{(\epsilon_3 - \epsilon_1)(\epsilon_3 - \epsilon_2)} \quad (4.11)$$

where ϵ_1, ϵ_2 and ϵ_3 are the cubic roots of

$$\epsilon^3 + \lambda \epsilon^2 + a \epsilon + a \omega_k = 0 \quad (4.12)$$

From the theory of equations, there will be 1 real and 2 complex roots or 3 real (with two equal) roots or 3 real roots depends on whether

$$a^2 \frac{(4a - \lambda^2)}{27} + \omega_k \left[\frac{-9a^2 \lambda + 2\lambda^3 a}{2 \times 27} \right] + \omega_k^2 \frac{a^2}{4} + \omega_k \frac{\lambda a}{2 \cdot 3} (2\lambda^2 - 9a)$$

larger or equal or smaller than zero respectively. The existence of one more additional root may offer a better comparison with MD experimental data.⁸

All the above cases have the distinct character that the n^{th} moment of the $\psi(t)$ exists for all n ¹⁶ i.e.

$$\langle t^n \rangle \equiv \int_0^\infty dt t^n \psi(t) < \infty \quad (4.13)$$

A very interesting investigation by Scher and Montroll¹⁸ to explain the anomalous transport in disordered amorphous system by using a $\psi(t)$ of the form

$$\psi_4(t) = 4a^2 e^{ka^2} \text{erfc}(a\sqrt{t}) \quad (4.14)$$

$$\rightarrow \frac{1}{\sqrt{\pi} a t^{3/2}} \quad \text{as } t \rightarrow \infty$$

seems to demonstrate that the following physical behavior implied by a $\psi(t)$ which has a long time tail¹⁸: At earlier time, the particles with such a $\psi(t)$ move by means of the relatively more probable short hopping time but as time increases, all particles eventually encounter at least one long hopping time and become temporarily stationary or trapped in a location.

Alley and Alder¹⁹ propose to modify the Fick's Law of diffusion in fluids where persistence of the velocity-velocity correlation function has been shown to be due to slowly decaying hydrodynamic field⁹. These fields are due to coupling between $\eta(\vec{r}, t)$ at two different space and time points mediated by a velocity field. It is shown that the frequency dependence diffusion coefficient $\tilde{D}(\epsilon)$ is

given in terms of both the $\psi(t)$ and the correlation function as

$$\tilde{D}(\epsilon) = \frac{\frac{\langle l^2 \rangle}{2} \tilde{\psi}(\epsilon)}{1 - \tilde{\psi}(\epsilon)} = \frac{1}{\epsilon} \widetilde{\langle v(t)v(0) \rangle} \quad (4.15)$$

$$\tilde{\psi}(\epsilon) = \frac{\frac{1}{\epsilon} \widetilde{\langle v(t)v \rangle}}{\frac{\langle l^2 \rangle}{2} + \frac{1}{\epsilon} \widetilde{\langle v(t)v \rangle}} \quad (4.16)$$

Suppose $\langle v(t)v \rangle$ given by (for all t)

$$\langle v(t)v \rangle = \frac{a}{\sqrt{\pi}t} - a^2 e^{-ta^2} \text{Erfc}(a\sqrt{t})$$

which has the right long time tail i.e.

$$\langle v(t)v \rangle \underset{t \rightarrow \infty}{\sim} \frac{1}{\sqrt{\pi} a t^{3/2}} \quad (4.17)$$

or

$$\widetilde{\langle v(t)v \rangle} = \frac{1}{1 + \frac{\sqrt{\epsilon}}{a}}$$

which gives

$$\tilde{\psi}(\epsilon) = \frac{1}{1 + \frac{\langle l^2 \rangle}{2} \epsilon + \frac{\langle l^2 \rangle}{2a} \epsilon^{3/2}} \quad (4.18)$$

which when put into the expression (4.3) gives

$$\frac{\tilde{\eta}_k(\epsilon)}{\eta_k(0)} = \frac{1}{\epsilon + \frac{\omega_k}{1 + A\epsilon + B\epsilon^{3/2}}} \quad (4.19)$$

A short time analysis results in

$$\frac{\eta_k(t)}{\eta_k(0)} \approx e^{-c_1 \omega_k t^{5/2}} \quad (4.20)$$

which explicitly shows a time-dependent rate. Kawasaki et. al¹⁴ give, by starting with the Navier-Stokes equations which also couples the density and velocity field, however a different time dependence

$$\frac{\eta_k(t)}{\eta_k(0)} \approx e^{-c_2 \omega_k t^{4/3}} \quad (4.21)$$

which has been shown to occur in too early a time to be observed in a real experiment.²⁰ We have shown here that by postulating a waiting time distribution which has a correct corresponding long time tail of the velocity auto-correlation function due to hydrodynamic interaction, one indeed obtains a time-dependent rate in the short time regime of spinodal decomposition.

V.- Generalization of MKR equation in the spatial domain

If one examines the intermediate equation¹²

$$\frac{\partial n}{\partial t} = - \frac{\beta R}{2\tau} \left\{ 1 - \int d\vec{r} \left(\frac{1}{(2\pi\lambda)^{3/2}} e^{-\frac{r^2}{2\lambda^2}} \right) e^{\vec{r} \cdot \nabla} \right\} \frac{\delta F}{\delta n} \quad (5.1)$$

which connects (1.20) and (1.22), the integral in \vec{r} -space is just

the Fourier transform of the $\psi(r)$ i.e. $\mathcal{F}[\psi(r)]$. After the procedure of linearization the rate w_k^{MKR} is related to the old rate w_k^{old} by

$$\frac{w_k^{\text{MKR}}}{k^2} = \left\{ \frac{1 - \mathcal{F}[\psi(r)]}{k^2} \right\} \frac{w_k^{\text{OLD}}}{k^2} \quad (5.2)$$

If $\psi_1(r) = \frac{1}{(2\pi\lambda)^{3/2}} e^{-\frac{r^2}{2\lambda^2}}$, the curly bracket $\{ \}$ is given by $(1 - e^{-\lambda^2 k^2}) / (\frac{\lambda^2 k^2}{2})$

so one recovers the results in section II. If $\psi_2(r) = a e^{-a|r|}$, $\psi(k) = a^2$ then $\{ \} = 1/(a^2 + k^2)$ and

if $\psi_3(r) = \frac{2}{\pi} \frac{a}{a^2 + r^2}$, $\psi(k) = e^{-ak}$

and $\{ \} = (1 - e^{-ak}) / k^2$
 $\xrightarrow{k \rightarrow 0} 1/k$

Finally if $\psi_4(r) = r^{-0.8}$, $\psi_k \sim k^{0.2}$ and $\{ \} \sim k^{-1.8}$

For $\psi(r)$ which has finite moments, the rate w_k/k^2 is finite at $k = 0$ whereas for $\psi(r)$ which possesses a longer tail, the rate is divergent at long wavelength limit. In Fig. 3, the MD result⁸ seems to indicate a faster rate as $k \rightarrow 0$. This approach, taking into account of a long range correlation between densities at two different points seems to be able to predict such a behaviour for the w_k/k^2 for small value of k .

V. Discussion

Of the two objectives of a theory of spinodal decomposition, we have generalised a new approach which stems from a unified description of MKR and we are able to give some new predictions of the spectrum of the early-stage of the unstable fluctuation. We have not touched on the description of coarsening as a function of time thus the crossover behavior²¹ of $k_m(t)$ is beyond our reach. At present we feel that the method of multiple time scale analysis, which has been successfully applied to problems in kinetic theory,²² may be helpful in providing another way to study this latter problem.

Though it is believed¹ that the distinction between nucleation and spinodal decomposition is not a sharp one, the existence of the spinodal however is firmly established in view of the MD data⁸ in the linear or early time regime. However Kawasaki and Onuki²³ still hold the view that there is no single data (actual or computer experimental) which establishes the existence of such a regime.

It is also clear from section I that all the theories have the same origin and differ only in the choice of $F[n]$. The theoretical basis put forward by Evans et. al⁶ seems to us the most satisfying one because of the fact that the role played by the direct correlation function becomes more and more important in present status of dense fluid state.

More work is expected to be done on the physical interpretation of the existence of more than one branch of the frequency spectrum both arising from Nonnenmacher¹¹ and our present study.

It is also to be pointed out that the upward curvature predicted by Cook⁹, Abraham⁸ and Evans et. al.⁶ are above the linear curve of $C-H^5$ whereas the Nonnenmacher¹¹ and the MD⁸ results seem to indicate the opposite i.e. the curvature should be below the linear curve so that the rate ω_k is less than exponential as remarked by Langer¹.

The unified approach of MKR¹² seems to indicate that unless there exists a system in which the correlation length λ associated with the variation of densities at two different points, is of the order of the size of cluster observed, otherwise nucleation and spinodal decomposition will occur as two separate events. However, if such a type of system can be found and investigated, then both the nucleation and the spinodal decomposition will contribute to the time evolution simultaneously.

Attempt to generalise (1.16) rather than (1.20) to a nonlocal Master equation generates some difficulty in applying the path integral method to obtain an equation corresponding to (1.2). The formal generalization of (1.20) to (3.1) does not bother us in view of the discussions following (3.1).

Experimental data seems to indicate the true presence of the non-Markoffian and nonGaussian nature of the spinodal decomposition but we believe that by allowing $\psi(r)$ and $\psi(t)$ to have longer correlation range, one has at least partially take these two natures into account even though it is still a phenomenological approach. This leads us to discuss the question of how good can the modeling of the kinetics of phase separation by a CTRW be? We do not claim

we have a sound basis for this approach but since any stochastic process¹⁶ can be described by $\psi(\vec{r}\vec{r}', t t')$, a distribution function of jump length and waiting time, irrespective of its specific form we believe that this approach is a powerful and flexible one. The remaining efforts will lie in the determination of the parameters in $\psi(\vec{r}\vec{r}', t t')$ from thermodynamics and their identifications with the experimental observables.

New predictions arise solely from a willingness to let the $\psi(\vec{r}\vec{r}', t t')$ to develop a long range either in space or in time. The spatial long range correlation is generally expected when phase transition²⁴ occurs e.g. from $e^{-r/\xi}$ to a power law dependence. The long time arises from the existence of additional collective modes in a dense system¹⁹. So our generalizations do find an analog in other physical phenomena. However much work is still needed to be done to establish the validity of the CTRW approach to explain and predict what is, or will be, observed in either nucleation or spinodal decomposition.

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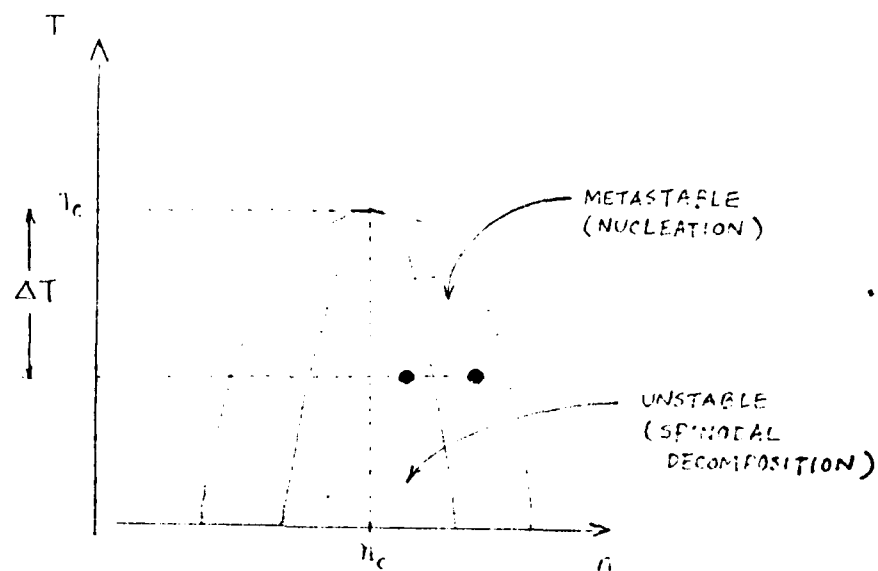


FIG. 1

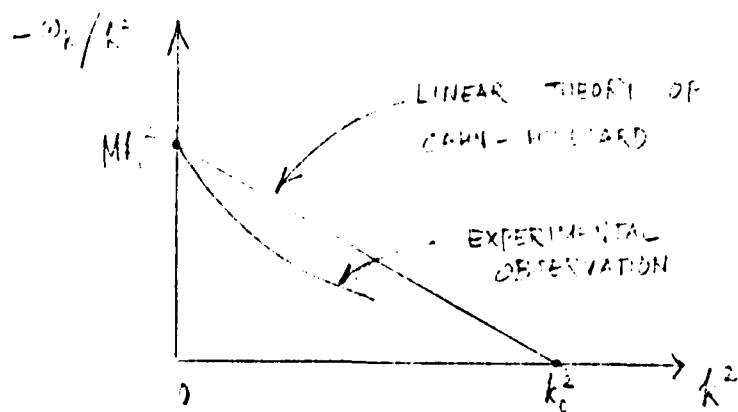


FIG. 2

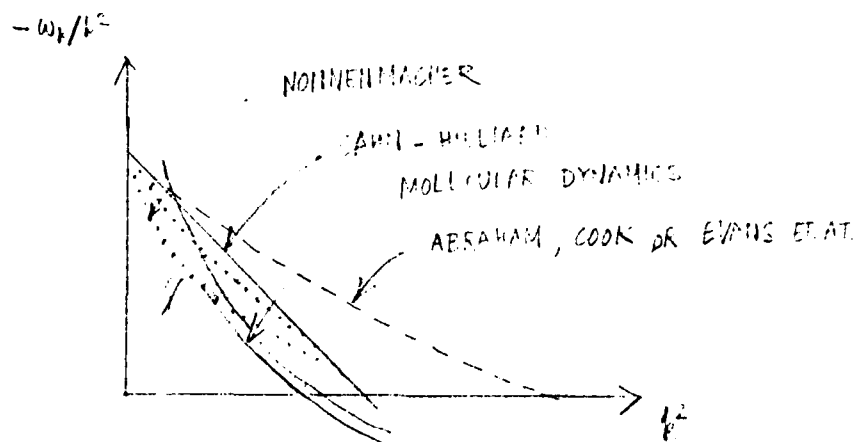


FIG. 3

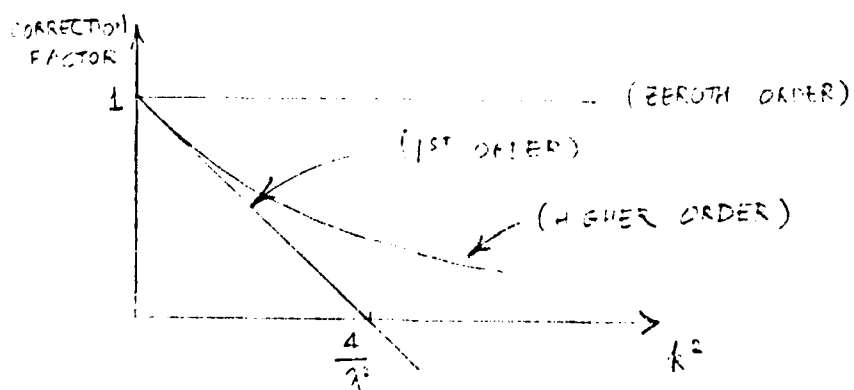


FIG. 4

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